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**Synthesis and Characterization of Cellulose fiber-silica
nanocomposites**

Master's thesis

Examiners: Prof. Kaj Backfolk

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Supervisor: M.Sc. Teija Laukala

ABSTRACT

Lappeenranta University of Technology

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Cellulose fiber-silica nanocomposites with novel mechanical, chemical and thermal properties have potential to be widely applied in different area. Monodispered silica nanoparticles play an important role in enhancing hybrids properties of hardness, strength, thermal stability etc. On the other hand, cellulose is one of the world's most abundant and renewable polymers and possesses several unique properties required in many areas and biomedicine.

The aim of this master thesis is to study if silica particles from reaction of sodium silicate and sulphuric acid can be adsorbed onto cellulose fiber surfaces via in situ growth. First, nanosilica particles were synthesized. Effect of pH and silica contents were tested. In theoretical part, introduction of silica, methods of preparation of nanosilica from sodium silicate, effect factors and additives were discussed. Then, cellulose fiber-silica nanocomposites were synthesis via route from sodium silicate and route silicic acid. In the experiment of route from sodium silicate, the effects of types of sodium silicate, pH and target ratio of silica to fiber were investigated. From another aspect, the effects of types of sodium silicate, fiber concentration in mixture solution and target ratio of silica to fiber

were tested in the experiment of route from silicic acid. Samples were investigated via zeta potential measurement, particle size distribution, ash content measurement and Scanning Electron Microscopy (SEM).

The Results of the experiment of preparing silica sol were that the particle size of silica sol was smaller prepared in pH 11.7 than that prepared in pH 9.3. Then in the experiment of synthesis of cellulose fiber-silica nanocomposites, it was concluded that the zeta potential of all the samples were around -16 mV and the highest ash content of all the samples was only 1.4%. The results of SEM images showed only a few of silica particles could be observed on the fiber surface, which corresponded to the value of ash content measurement.

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LIST OF SYMBOLS AND ABBRELIATIONS

ABBREVIATIONS

BC Bacterial cellulose

$C_6H_8O_7$ Citric acid

$C_2H_2O_4$ Oxalic acid

EC Electrical conductivity

HCl Hydrochloric acid

H_2SO_4 Sulphuri acid

LbL Layer-by-layer

NaOH Sodium hydroxide

PMMA Polymethylmethacrylate

PEO Poly(etheleneoxide)

SEM Scanning Electron Microscope

SEI Secondary electron imaging

TEOS Tetraethoxysilane

SYMBOLS

Si-O-Si Siloxane bonding

Si-OH Silanol bonding

T Temperature, °C

MPa Pressure

GPa Pressure

1 Introduction

The search for renewable resources for production organic-inorganic hybrids has steadily increased in recent years. For hybrids have interesting mechanical, chemical and thermal properties, fibers have been widely used as organic phase in hybrids. Silica particles which are one of the most abundant materials with various morphologies are easily compatible with different kinds of material. Furthermore, if fibers and silica particles can be compressed as organic-inorganic hybrids, it can be demonstrated that they both have advantages of organic materials and strength of inorganic phases.

The research of cellulose fiber silica nanocomposites have been developed very fast in recent years. The most important effort is focused on how to obtain desired nano scale of silica particle and uniform surface with advanced methods/1/. There are mainly three methods to synthesize cellulose fiber-silica composites: so-gel, layer-by-layer assembly method and mimicking biomieralization. Sol-gel process is the most used to prepare organic-inorganic hybrids, especially to produce silica hybrids. The layer-by-layer assembly method is based on the electrostatic interaction between polymers/1/. The mimicking biomieralization methods are different from searching of normal cellulosic composites because most of normal cellulose is not soluble in normal solvent/2/. Bacterial cellulose hydro-gel is commonly applied as starting materials.

Typically the starting materials for silica particle are silanes, e.g. Tetraethoxysilane (TEOS). However, sodium silicate as cheaper silica resources should be widely used to produce silica hybrids. Moreover, although there are many different kinds of production methods to prepare cellulose fiber-silica composites, most of they are complicated and long time process. In this case, it

needs to consume much energy and its efficiency is quite low.

In this study, cellulose fiber-silica nanocomposites were prepared from sodium silicate and cellulose via in situ growth. First, nanosilica particles were prepared via silica sol. Silica particles were characterized with particle size distribution and zeta potential measurement. The most suitable conditions for preparing nano size silica particles with fiber were determined. Second, cellulose fiber-silica nanocomposites were synthesis via route from sodium silicate and route from silicic acid. After preparation, samples were investigated with zeta potential measurement, ash content measurement and Scanning Electron Microscopy to analyze the results of synthesis.

2 Synthesis of nanosilica

2.1 Silica

Silica is one of the most abundant and most complex materials, existing no matter as being synthetically produced or natural materials, for example fumed silica, fused quartz, crystal, amorphous, silica gel and silica sol. Colloidal silica is suspension solution, which contains spherical and amorphous silica particles. Uniform particle size of colloidal silica is approximately from 5 nm to 1500 nm, typically from 5 nm to 100 nm /3/.

2.1.1 Properties

Silica can be assumed a polymer of silicic acid, which contains cross-linked SiO_4 units, so that molecular formula of silica is SiO_2 . As can be seen in Figure 1, two molecules of silica shared one oxygen atom. Si-O-Si bond angle is displayed in Figure 1 as well /4/. Moreover, the density of colloidal silica particles is between

2.1 to 2.3 g/cm³. Silica is in different forms in nature, such as sand, quartz and glass etc. Colloidal silica is the form of colloidal state of silica particles in liquid phase. In colloidal silica, silica particles will be linked together in both small size (1 nm) and sufficiently large size (1 mm). No matter what kind of the size, surface forces and van der Waals attraction are the most common interaction forces between molecules.

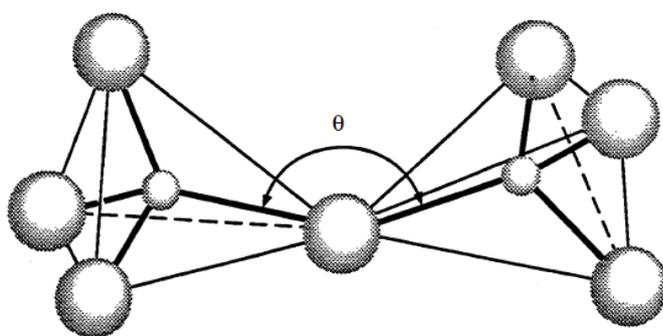


Figure 1. Schematic representation of adjacent SiO_4 tetrahedra that shows the Si-O-Si bond angle, small circle, Si, large circle, O /4/

2.1.2 Stability

Colloidal stability is very important parameter when applying colloidal silica, no matter in mechanical, chemical or thermal area. Stability in colloidal state means that colloidal particles do not settle in short time or bunch up to form larger cluster and then settle after a short period /5/. In this case, colloidal silica is easy to link together with other particles by aggregation, coagulation, flocculation, gelation etc. If particles link together to form larger clusters or three dimensional networks and start to settle down in liquid phase, even become gel form, it means that silica sols have lost their stability.

Even though both gelation and coagulation will make silica sols lose their stability,

they are basically different with each other. When a sol is gelling, colloidal silica particles link with each other one by one and form long chains. As a result, sol will become more viscous and finally look like soft solid materials. On the other side, coagulation somehow means that precipitation. Silica particles will link with each other and form clusters. When clusters become large enough, they will settle down, so that sediments in the liquid phase can be seen at the bottom of containers. Figure 2 /6/ shows the difference between a sol, gel and precipitate of silica.

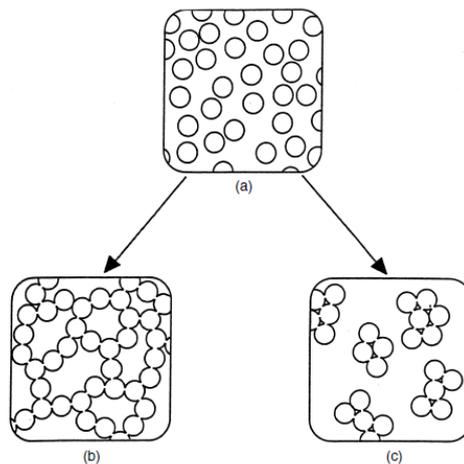


Figure 2. Silica gel versus precipitate: (a) sol, (b) gel, and (c) flocculation and precipitation /6/

Her /6/ distinguished the different ways in which silica particle in colloidal state link together or aggregate in the following manners:

1. Gelling: particles in branched chain linked with each other, then the overall medium becomes viscous and forms a coherent network by solidifying, retaining the liquid.
2. Coagulation: particles connect together to form clusters, which the concentration of silica is larger than in the sol. As a result, aggregation of silica

clusters will settle down by gravity force in liquid phase.

3. Flocculation: silica particles come together with linkage of the sufficiently long flocculating agent so that the aggregated structure remains open and voluminous.

4. Coacervation: The significantly hydrophobic material layer surrounds outside the silica particles. In this case, particles aggregate because it is immiscible in the aqueous phase.

It is also known that silica sols pH strongly affects the stability. In spite of the fact that the isoelectric point of silica solutions is $\text{pH}=2$, the particles tend to disperse around this pH value. Colloidal silica is metastable at around $\text{pH}= 2-3$. Silanol condensation reactions will become faster and faster when pH increases from 2 till 5-6, where the colloidal silica is the most unstable. From pH 5-6 to be higher, surface charges increase, so that electrostatic repulsions between particles increase. As a result, colloidal silica become more stable with higher pH value from 5-6.

2.1.3 Application

Colloidal silica can be applied in many fields as listed below:

1. In paper industry, colloidal silica can be applied as a drainage aid [7]. Colloidal silica increases the dry strength of the paper because the amount of cationic starch will be higher by adding colloidal silica as sizing agent.

2. Normally, colloidal silica can be used in models for investment casting.

3. Recently, it has been used in the different industries because silica is an inorganic material which has high strength and hardness. For example, used as stiffener reagent in hard coating, binder in inorganic paint, [8-12] and especially as

an abrasive particle to be adding in chemical or mechanical polishing slurry /13-15/.

4. Activate silica, one form of soluble silica, is usually applied in water industry as surfactant, where it helps alum-induced flocs to settle down /3/. In addition, silica can be used for flocculating, coagulating, dispersing, stabilizing. Furthermore, liquid silicon dioxide can be often applied as a juice or wine fining agent.

2.2 Methods of synthesis of nanosilica

The process of colloidal silica has been investigated since 19th century /3, 16–23/. Tetraethyl orthosilicate (TEOS) is one of the most common raw materials on silica production. Actually, sodium silicate as another kind of silica raw materials, has many benefits, such as a slow grow rate, low cost, possibility of particle surface modification etc. What is more, sodium silicate can be widely applied in many fields, such as adhesives, coatings, detergents, etc /24-27/. Recently, the use of silica as inorganic material to synthesize well-organized material has attracted many researchers interest /28-31/.

Normally, SiO₂ sols are produced by the neutralization of sodium silicate (Na₂O • nSiO₂, also called water glass) and sulfuric acid (H₂SO₄) as shown in Eq.(1), which is an easy and convenient progression for industrial mass production:



Yoshida /3/ indicated that methods of producing colloidal silica which is made from sodium silicate included peptization method, acid-neutralization method and ion-exchanging method.

2.2.1 Peptization method

As it can be seen in Figure 3 /3/, precipitated silica gel with sodium sulfate and other salts is formed by neutralization of hydrochloric acid or sulphuric acid and water glass solution. Then silica gel is washed with water to remove salts. Third, water and sodium hydroxide solution are added into wet gel to obtain silica gel slurry. After heating in autoclave at about 120-150 °C, peptization happens and silica sol is obtained. However, it is difficult to obtain uniform desired silica particles or high purity by peptization method.

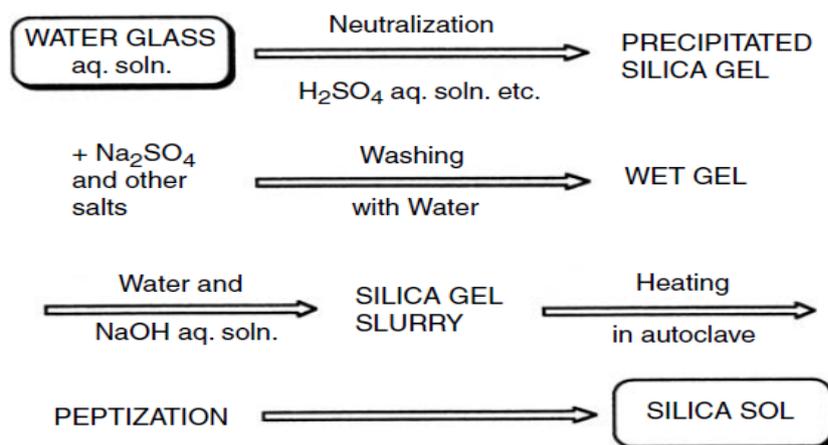


Figure 3. Peptization method of preparing silica sol /3/

2.2.2 Acid-neutralization method

Figure 4/3/ shows that silica sol with sodium sulfate and other salts are prepared by partial neutralization and particle growth of adding water glass solution into dilute sulphuric acid or hydrochloric acid. Salts can be removed with dialysis and electrodialysis. Then, silica sol will be concentrated with evaporation and ultrafiltration. In recent years, this method is used more and more widely because of development of filtration technology.

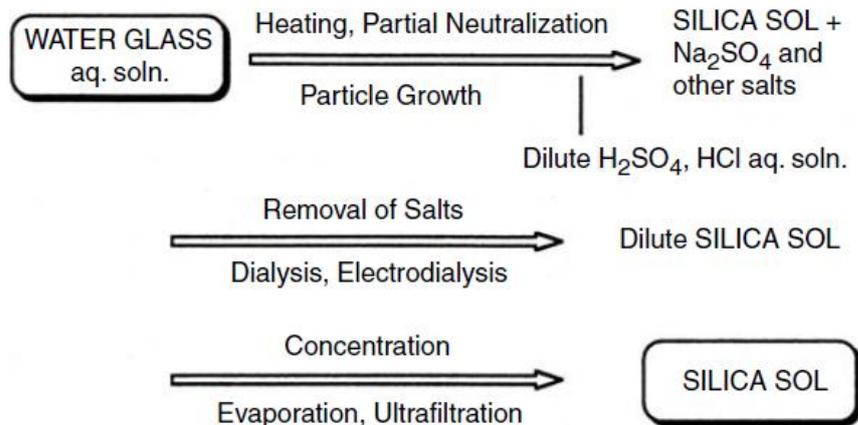


Figure 4. Acid-neutralization method of preparing silica sol /3/

2.2.3 Ion-exchanging method

Recently, ion-exchanging method is the major method of production of silica sols. This method basically includes three parts.

As shown in Figure 5/3/, polysilicate anion will form by adding water to water glass solution to dilute sodium silicate solution until SiO₂ concentration reach to 2-6 wt%. Then, cation exchange resin is used to remove ion in de-sodium ion stage. After this stage, oligomer will form in active silicic acid solution with 2 nm SiO₂ particles. Next, nucleation, particle growth, polymerization happen to form dilute silica sol. SiO₂ particle size is around 4-100 nm in this silica colloidal. In the end, silica sol is concentrated with 15-60 wt% SiO₂.

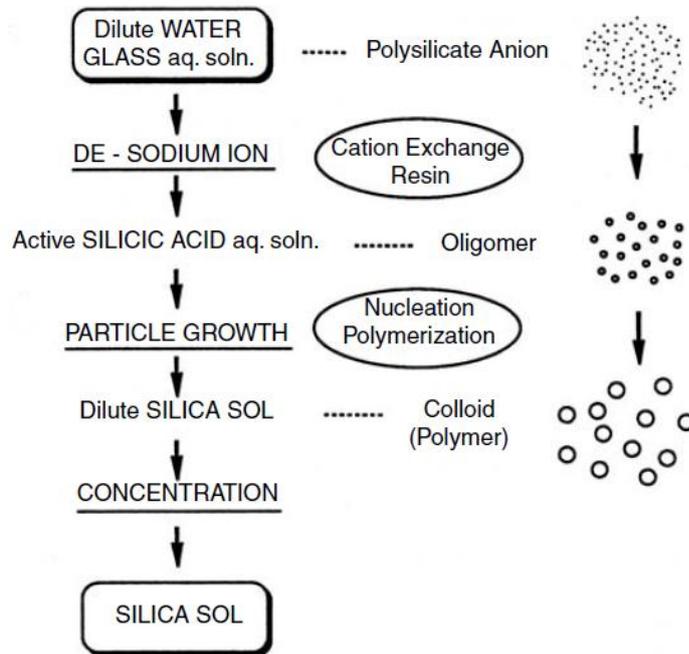


Figure 5. Preparation of silica sol with ion-exchange method /3/

2.3 Factors and additives that have effect of synthesis of nanosilica

There are many factors that have great effect on synthesis of silica particle, such as silica surface area, particle size of produced silica, reaction rate. Effect of pH, reaction temperature, silica source concentration, acid, salt concentration will be further discussed as follows.

2.3.1 Effect of pH

The pH has great effect on not only porosity but also particle size of silica particles. Tzong-Horng Liou/32/ found that pH strongly affect the surface area of silica particles. Surface area decreases with increasing of pH value, i.e. the silica obtained at pH 9 had the lowest surface area (237 m²/g), while the highest surface area (634 m²/g) was obtained at pH 3. When pH increases from 3 to 9, as shown in the following two paths, a condensation reaction may happen during gel

formation, resulting in increasing particle size and porosity /33/.



where, the OH^- plays an important catalyst role. In the acid regime, reduced pH leads to changing of siloxane bonding (Si-O-Si) to silanol bonding (Si-OH) and gel formation is slow.

As can be seen above, the OH^- increases the reaction of equation (2). In the acid solution, decreasing of OH^- will result in more siloxane linkages (Si-O-Si) change into silanol groups (Si-OH), so that colloidal suspension becomes more stable. As a result, more small particles will form, so that surface area of silica will be higher. In the basic solution, reaction will reverse so silanol groups will change into siloxane

In this case, silica is composed of small particles and therefore, possesses high surface area. In the basic regime, surface silanol bondings tend to form siloxane bondings. Siloxane linkages create negative charges and increased electrostatic repulsion between silica particles /34/.

The charge develops silica particles to connect together more, so that particle size becomes larger when pH increases. That is why higher porosity and lower surface area will be obtained in this situation.

2.3.2 Effect of temperature

Temperature is another factor which will influence the production of silica. The effect of temperature on surface area of silica sol produced at pH 7 was studied by

Tzong-Horng Liou /32/. Surface area increased due to fast growth of silica reaction when temperature increased from 20 °C to 50 °C. However, when the temperature is high enough, surface area decreased with increasing temperature as gelation reaction is faster than silica particles growth. Silica network became thicker and pores become smaller. As a result, surface area of silica particles decreased. The increasing temperature helps particle to further grow, resulting in smaller mean particle size of silica prepared in lower temperature than that produced in higher temperature. Moreover, an accelerating effect of temperature on gelation has been observed in previous studies /35/.

2.3.3 Concentration of silica source

As silica was produced from sodium silicate, the concentration of sodium silicate has a great influence on synthesis of silica sol. Concentration of silicate significantly has an effect on the surface area and particle size, because nucleation and growth reaction of silica particles when preparation of silica. At lower silicate concentrations, the surface area of silica usually increases until a maximum surface area reaches /32/. Because, when sodium silicate solution is diluted enough, the silica surface area is low. Increasing concentration of sodium silicate leads to forming more cores, so that surface area increases in this case. Gelation rate increases with higher concentration of silicate. Increasing growth rate of silica particles on the pore wall results in decreasing of pore diameter, therefore, reduces silica surface area. M.M. Hessian /36/ stated that when silicate concentrations increased from 10% to 30%, particle size of silica reduced. The particle size and growth rate increased as higher sodium silicate concentration which led to higher rate of nucleation.

More sodium silicate with high concentration leads to saturation of silicic acid, resulting in connection of monomer polymer. On the other hand, it can be

concluded that deposition time of silica also increases when sodium silicate becomes more diluted/37/.

2.3.4 Effect of acid on silica production

Different kinds of acids affect the silica surface area. Tzong-Horng Liou /32/ also studies the function of acid treatment, including sulphuric (H_2SO_4), hydrochloric (HCl), citric ($\text{C}_6\text{H}_8\text{O}_7$), oxalic ($\text{C}_2\text{H}_2\text{O}_4$) acids on the formed surface area. When producing silica with citric acid, surface area reached a minimum. When samples were prepared by using sulphuric and oxalic acids, the surface area increased. Moreover, a maximum surface area of silica was obtained with HCl. On the other hand, the effect of sulfuric acid concentration on silica particle size has been studied by M.M. Hessien /36/. However, from results of this study, showed that the particle size of prepared silica particles was insignificantly affected by concentration of sulphuric acid in the range from 4% to 20 %.

2.3.5 Effect of salt concentration

The dehydration reaction of silicic acid will happen in the alkali solution/3/. In this case, silica form nuclei first and thus particle grows further. Therefore, increasing salt concentration means increasing sodium ion concentration, resulting in larger particle size of produced silica /35/.

Furthermore, other parameters would have an effect on the formation of colloidal silica, such as $\text{SiO}_2:\text{Na}_2\text{O}$ ratio, the titration rate, reaction time, stirring speed. In order to get the most desired silica sol, experiment should be taken under optimum condition. In my study, the easiest method of synthesis under mild conditions and common raw materials were used for industrial application in the future. Titration of sodium silicate and sulphuric acid simultaneously to water

vessel with 200 rpm stirring speed and desired temperature, while keeping pH of vessel constantly.

3 Synthesis of cellulose fiber-silica nanocomposites

3.1 Cellulose fiber-silica composites

Organic-inorganic composites are a relative new type of exciting hybrids with novel properties, such as favorable electrical, thermal, optical and mechanical properties /38/. The properties of organic/inorganic hybrid materials are beneficially affected by adding inorganic component to the organic polymer matrix. The inorganic component is usually brittle, with heat resistance, surface strength and hardness, whereas the organic one, although thermally unstable, but contributes to the hybrid of flexibility, toughness, and low density /39, 40/. The properties of nanocomposites depend not only on the individual performance of both components but also on their interfacial and morphological characteristics. Properties of these composite materials are not the simple addition of their individual ingredients, but the contribution of the inner interfaces could be dominant /41/.

Cellulose is a biopolymer which is readily available, renewable and abundantly found in nature, typically combined with hemicelluloses and lignin in the cell wall of plants /42/. Hydrogen bonds are indicated the basis of cohesion between cellulose molecules. It is generally believed that intramolecular hydrogen bonds not only improve chain stiffness, but also allow the linear polymer molecules to assemble in sheet-like structures (Figure 6) /43,44/. Both the microscopic and macroscopic properties of cellulose are expected to be considerably influenced by such structural anisotropy. Cellulose, as an abundant biodegradable and renewable natural polymer, gives organic support for organic/inorganic hybrid materials /46/.

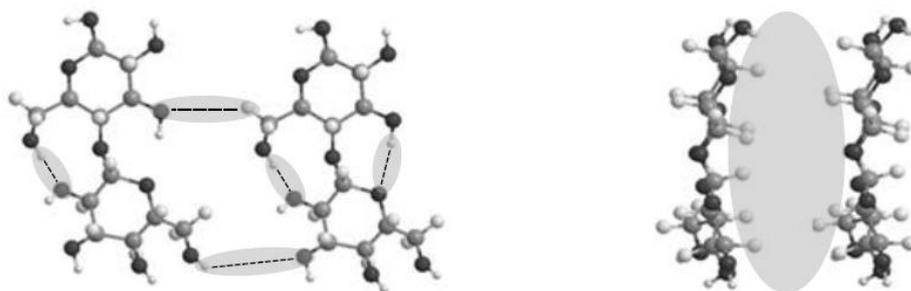


Figure 6. Hydrogen bonds between cellulose molecules/44/

Cellulose fiber-silica composites are the combination of inorganic silica nanoparticles and the most abundant renewably natural polymer. Degradation temperatures of cellulosic materials are relatively low and its mechanical properties will dramatically lose upon moistening. To overcome these shortcomings, one promising way is surface modification by introducing an inorganic component /46/. Silica, as dispersed particles of the inorganic phase, could improve the hardness, thermal stability, lipophilic behavior and transparency /47/. In this case, monodispersed silica nanoparticles with uniform shape, composition, and size could be widely used in industries such as the production of pharmaceuticals, catalysts, ceramics and pigments /48/. The demand for well-defined silica nanoparticles increases constantly, as high-tech industries such as pharmaceuticals, biotechnology and photonics offer a huge demand for materials of this type /49, 50/. What's more, as one of the most abundant polymers in the world, cellulose has several unique properties which are required in biomedicine and various technical areas /51/. Cellulose and its derivatives are quite applicable raw material for synthesizing organic-inorganic hybrids /52/.

3.2 Methods of synthesis of cellulose fiber-silica composites

As being novel material, cellulose fiber-silica hybrids have been synthesized with different methods from different kinds of fiber and silica sources. There are

mainly three methods to prepared cellulose fiber-silica composites with interesting mechanical, chemical, thermal and electrical properties.

3.2.1 sol-gel method

A rather flexible and high efficiency technique - sol-gel process is used in the synthesis of a large proportion of organic-inorganic hybrids recently reported. Because cellulose fiber-silica composite is one kind of organic-inorganic hybrids, it means that sol-gel process can be used to prepared cellulose fiber-silica mixture. Moreover, M.A.Tshabalala et al. /53/ has used sol-gel for depositing hydrophobic polysiloxane coatings onto wood. Sulphite pulp can be modified with water soluble silicon-containing compounds /54/ by using a sol-gel method to enhance the hydrophobicity of the final hybrid materials. Mostly by hydrolysis of metal alkoxides and then condensation reactions the inorganic phase can be obtained. Xiaonqiong Chen et al /55/ prepared monodispersed silica nanoparticles by using a two-step method with hydrolysis and condensation. As can be seen in Figure 7, a dual-scaled surface with cellulose fiber and silica was generated through in-situ growth of silica nanoparticles on cotton fabrics. This kind of surface processes superhydrophobic property.

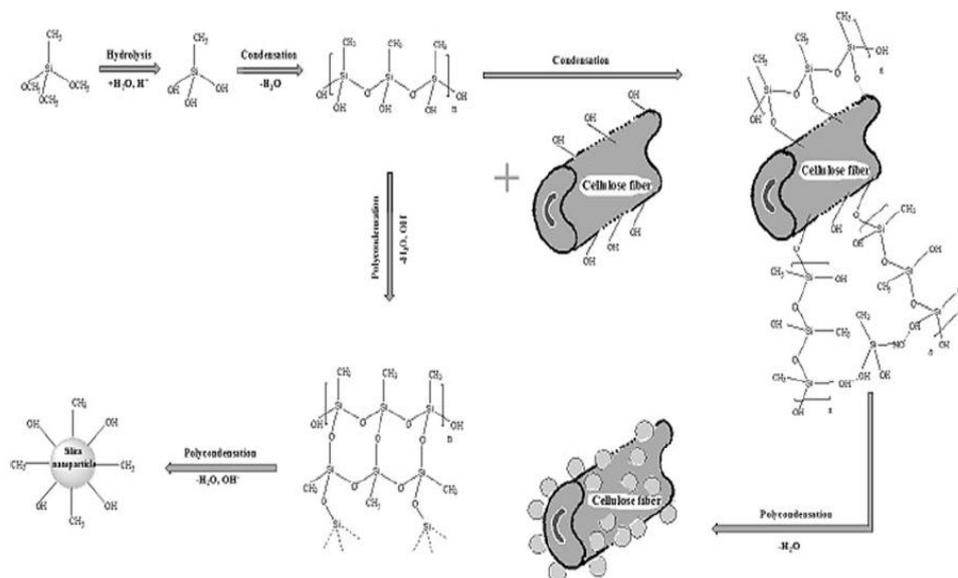


Figure 7. Reaction process of production of silica particles and silica adsorption on cellulose fiber surface/55/

3.2.2 Layer-by-layer assembly method

Electrostatic interactions between ions are the base of the layer-by-layer (LbL) assembly method.

Adsorbing oppositely charged ions onto the solid surface is the main step of this method.

Multicomposite films can be easily assembled with this technique. The interaction of each layer is based on oppositely charge in its layer-by-layer construction. The inorganic compounds can be adsorbed onto the surface due to its interaction between each layer /56/.

In Ricardo J.B. Pinto /1/ study, novel SiO₂/cellulose nanocomposites were obtained with this technique. As can be seen in Figure 8, the discrete and morphological well-defined SiO₂ nanoparticles were obviously found on the

cellulosic fibers surfaces.

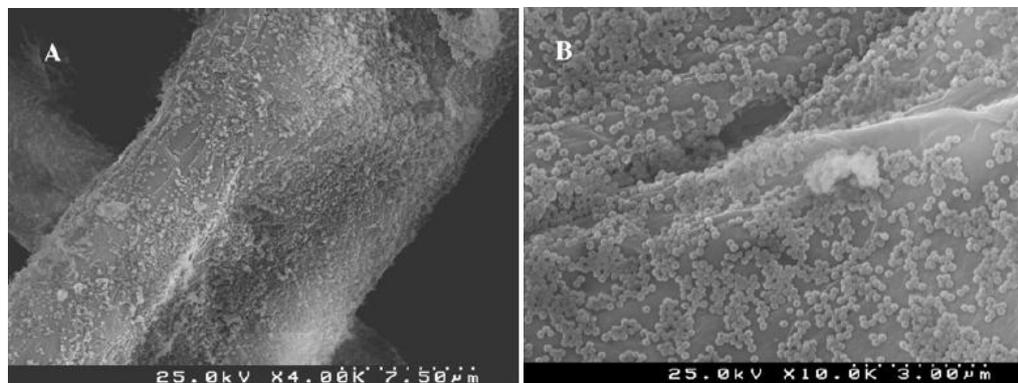


Figure 8. SEM images of cellulose fiber-silica nanocomposites with LbL technique /1/

3.2.3 Mimicking biomineralization

In nature, there are many interesting composite material produced by biomineralization.

Composite materials having excellent properties are mostly found in natural materials, which are produced by natural biomineralization. Typical examples of biocomposites are bones, eggs, shells and teeth. In plants such as rice, grasses, amorphous silica will be on matrix via biomineralization. In recent year nanotechnology has been used to simulate much interesting research in this area and many investigations have been made to produce such biocomposites by using mimicking natural biomineralization. By using a method of forming oxide into a soft-tissue matrix from soluble precursors, Sobon et al. /57/ prepared PMMA/magnetite and polymethylmethacrylate (PMMA)/ ferric oxide composites. Furthermore, poly(etheleneoxide) (PEO)/Cds situ composites were obtained by Bianconi et al. /58/ through mimicking the biosynthetic mechanisms. Through a polymer matrix, morphology crystal size and orientation of Cds can be designed.

Cellulose/silica hybrid can be produced in rice plant via mimicking the biomineralization. On the other hand, Hideaki Maeda /2/ has prepared a cellulose/silica hybrid from bacterial cellulose (BC) hydro-gel matrix. Figure 8 shows the procedure of producing of BC/silica hybrid sheet. The silanol solution was first produced from tetraethoxysilane (TEOS), BC hydro-gel was then immersed into it. After that, silica which is transferred from silanol went into the BC hydro-gel matrix. In the rice plants, the modulus of tensile strength and elasticity was usually 25-88 MPa and 3.5GPa at 25 °C, respectively, while the modulus of dry BC/silica hybrid has developed to 185 MPa and 17GPa at 25 °C, suggesting a stronger structure of BC hybrid.

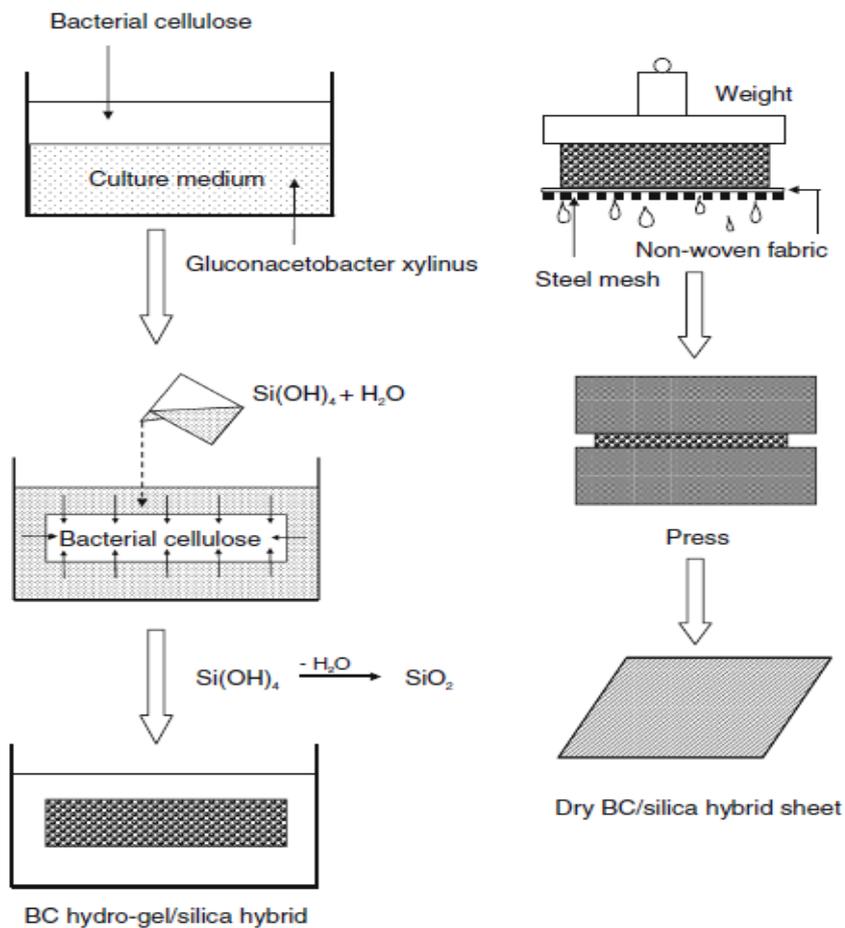


Figure 9. Procedure of producing of BC hydro-gel/silica mixture and dry BC/silica mixture /2/

3.3 Applications of cellulose fiber-silica composites

More than 200 million ton of unbleached/ bleached pulp was produced from paper industry all over the world every year. Although this pulp is mainly used for papermaking, the production of modified fibers, coatings, films, etc has become more and more, for their low production cost and high economic margin /59/. Cellulose fiber-silica with advanced mechanical, chemical and sorption properties is considered a potentially alternative application of fibers. Cellulose fiber-silica hybrids can be applied in different fields with novel properties and excellent performance.

3.3.1 Rigid material

The introduction of a silica network on cellulosic materials obviously enhanced their bending strength. With higher modulus of elasticity and tensile strength, cellulose fiber-silica can be made as rigid material to resist structural deformation.

3.3.2 Super hydrophobic surface

In cellulose fiber-silica hybrids, silica particles were captured into the organic network so that it converted to structural network. Moreover, the surface with microscaled roughness of cellulose fiber and nanoscaled roughness of silica was generated. Which is similar with lotus leaves, such a surface can be applied to resist water very well. A stable superhydrophobic surface was obtained by immersing cellulose fiber substrates into ethanol solution containing silica nanoparticles/60/. Xianqiong Chen/55/ has prepared monodispersed silica nanoparticles on fiber surface with a two-step method with hydrolysis and condensation. From their SEM images (Figure10), some obvious changes can be demonstrated on the surface of fiber. There are some particles can be found on the

treated fiber surfaces, while untreated cotton is relatively smooth.

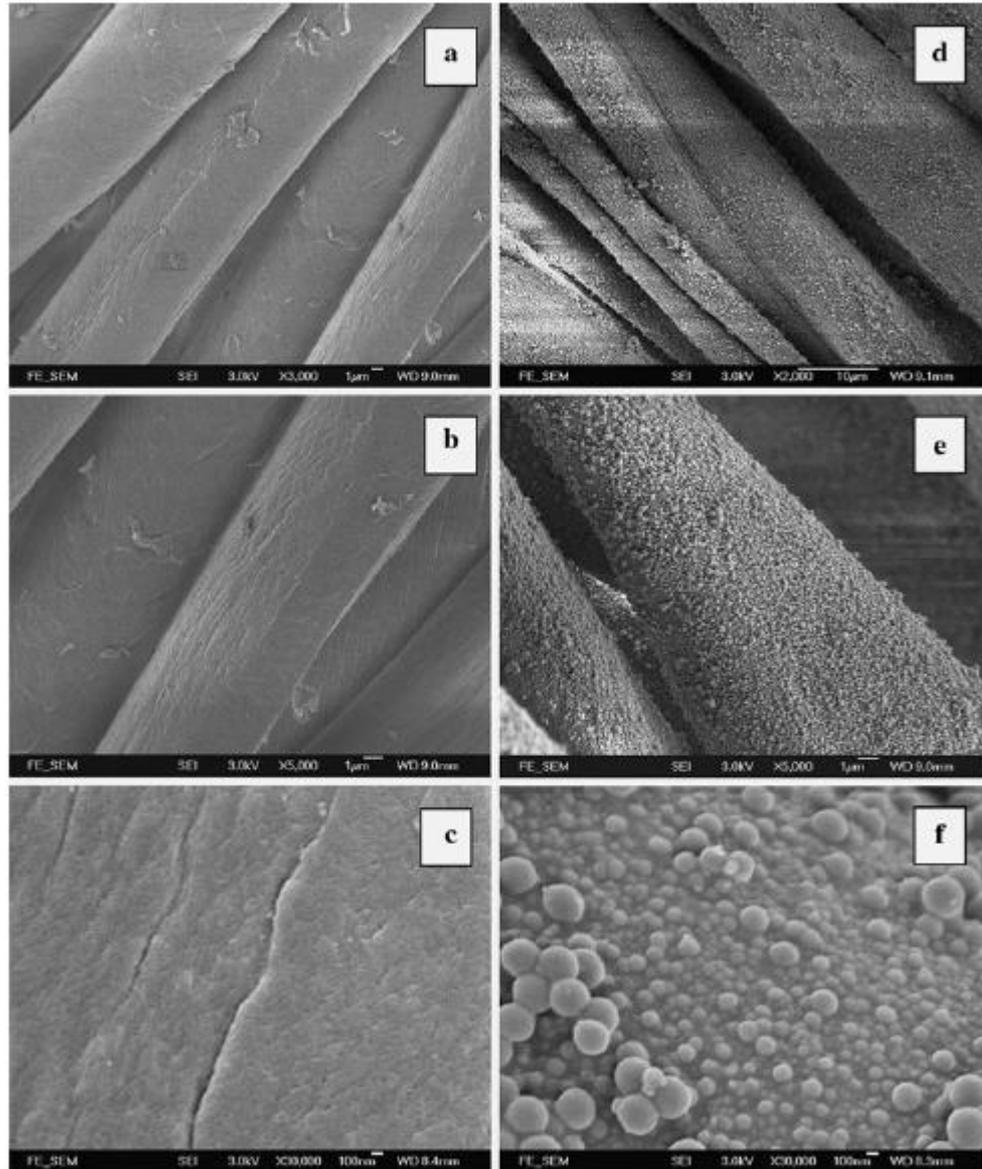


Figure 10. SEM images of (a) fiber surface of a magnification ($\times 3,000$), (b) a magnification ($\times 5,000$), (c) a magnification ($\times 30,000$) and (d) silica particles adsorbed onto the fiber surface of a magnification ($\times 2,000$), (e) a magnification ($\times 5,000$) and (f) magnification ($\times 30,000$)/55/

3.3.3 Thermal insulation material

The thermal conductivity of these mixture materials bear comparison with insulation foams which are commercially available [61]. In this case, cellulose is renewable abundant material while foam is product from gasoline industry, which is cannot be recycled and also not environmentally friendly.

EXPERIMENTAL PART

4 Materials and Methods

4.1 Raw materials

Chemicals used in this study were sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=3.20\text{-}3.40$, with measured solid content of 43% and $\text{SiO}_2:\text{Na}_2\text{O}=2.00\text{-}2.10$, with measured solid content of 50%, PQ Finland Oy), sodium hydroxide ($\text{NaOH}\geq 99\%$, Merck), sulphuric acid (95-97%, Merck) and cellulose fibers(, JRS ArboceI UFC 100, with mean particle size 8 μm according to the supplier, J. Rettenmaier & Söhne GmbH+CO.KG.)

4.2 Synthesis of silica sol and cellulose fiber-silica nanocomposites

In this study, a sol of nanosilica was synthesized in different pH using sodium silicate and sulphuric acid to compare the effect of pH and silica content on particle size distribution and zeta potential of silica. Then, cellulose fiber-silica composites were synthesized with routes from sodium silicate or silicic acid to investigate silica particles on the fiber surface.

4.2.1 Synthesis of silica sol

Silica sol: Sodium silicate was diluted into desired concentration with sodium hydroxide solution which had the same pH value with the sodium silicate. The pH value of batch vessel was 9.3 or 11.7 with sodium hydroxide and water, sodium silicate and sulphuric acid were then titrated simultaneously into the batch vessel under desired temperature and constant stirring rate of 200 rpm. During the titration, pH value of batch vessel maintains was kept around 9.3 or 11.7 by controlling titrating speed and amount of sulphuric acid. Different samples were

taken out after different amount of sodium silicate were titrated.

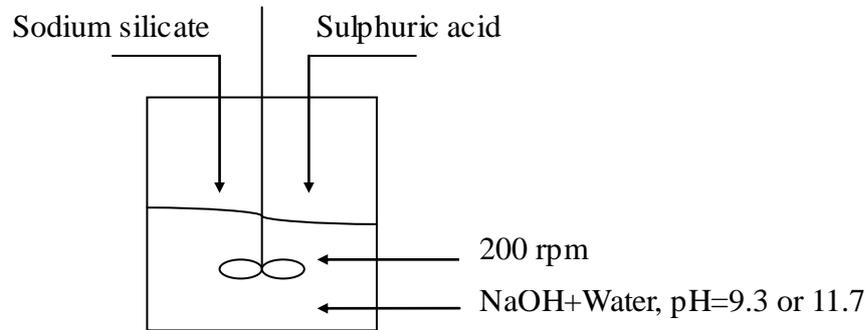


Figure 11. Process of preparing silica sol

4.2.2 Synthesis of cellulose fiber-silica nanocomposite

Route from sodium silicate:

1 wt-% fiber solution was used in the batch vessel. The pH value of suspension was 3.0 or 9.3 and temperature was 25 °C. 5M sulfuric acid and undiluted sodium silicate were titrated simultaneously into the batch vessel, while keeping pH of vessel at constant. The samples were taken out at different titration delay time. The sample of silica was then filtered. And after filtration, the sample was washed with ca. 1 liter of water by breaking the cake into water, stirring and then filtering again. The wet cake could be obtained after washing and filtration. A part of the wet cake was used in zeta potential measurement. The dry cake was obtained after the wet cake was put into the oven at 105 °C for 24 hours. After that the dry cake was used to be measured with ash content and SEM.

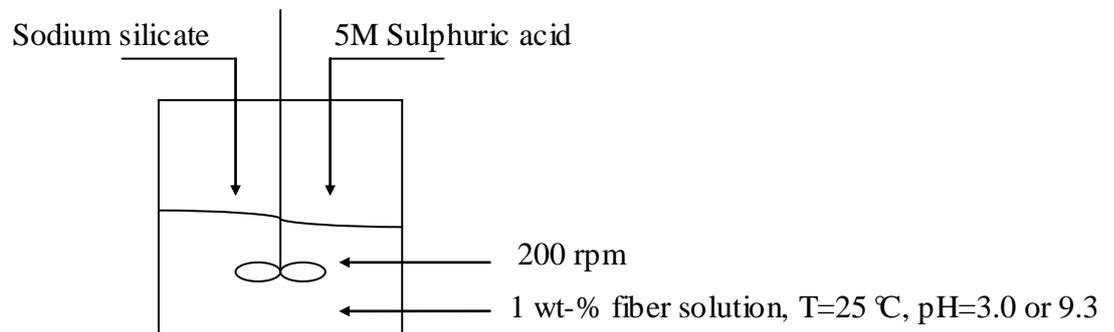


Figure 12. Route from sodium silicate of synthesis of cellulose fiber-silica nanocomposite

Route from silicic acid:

Fiber, undiluted sodium silicate and sodium hydroxide were mixed to make fiber-sodium silicate mixture solution. The pH value of vessel was 3.0 with water and sulfuric acid and temperature was 25 °C. Keeping pH of vessel at constant, 5M sulfuric acid and mixture solution were titrated simultaneously into the batch vessel until concentration of fiber in the vessel reach 1 wt-%. The sample was filtered. After filtration, the sample was washed with ca. 1 liter of water, stirred and then filtered again. The wet cake could be obtained after washing and filtration. Then the wet cake was used in zeta potential measurement. The dry cake was obtained after the wet cake was put into the oven at 105 °C for 24 hours. After that the dry cake was used to be measured with ash content and SEM.

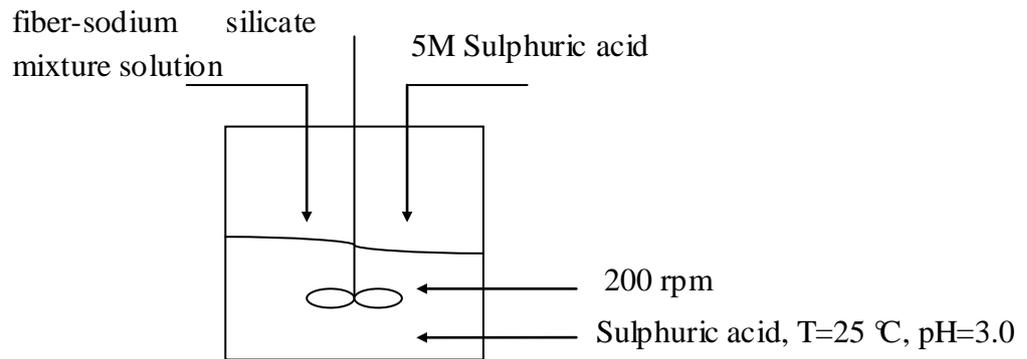


Figure 13. Route from silicic acid of synthesis of cellulose fiber-silica nanocomposite

4.3 Characterization of samples

Silica sol samples were measured with particle size distribution and zeta potential. On the other hand, cellulose fiber-silica samples were measured with zeta potential, ash content and Scanning Electron Microscopy (SEM).

4.3.1 Particle size distribution measurement

Particle size distribution measurements were performed using a Zetasizer Nano ZS (Malvern) instrument. All the samples were diluted to 5 g/l by adding sodium hydroxide solution.

4.3.2 Zeta potential measurement

Zeta potential measurements were performed using a Zetasizer Nano ZS (Malvern) instrument. Silica sol samples were diluted to 5 g/l by adding sodium hydroxide solution. Cellulose fiber-silica samples were diluted with sodium chloride solution to 0.3 g/l and electrical conductivity (EC) 1.3 mS/cm.

4.3.3 Ash content measurement

Ash content of cellulose fiber-silica samples were measured according to standard Tappi T 413 with combustion at 900 °C using a muffle furnace (Vulcan A-550, NEY).

4.3.4 Scanning Electron Microscopy

The surface morphology of silica particles coated on fiber surface was investigated by SEM (JEOL, JSM-5800, Tokyo, Japan) using secondary electron imaging (SEI) operating at 10.0 kV. The samples were sputter-coated with cold prior imaging.

5 Results and Discussion

5.1 Producing silica sol

As can be seen as above, silica sol was prepared in pH 9.3 and pH=11.7, T=25 °C with different silica content. In pH 9.3 particle size increased with increasing silica content from 5 g/l to 20 g/l.

When the silica content reached 20 g/l, the average particle size was more than 300 nm. However, as can be seen in Figure 15 when the silica content was increased from 5 g/l to 15 g/l, silica particle reduced and was below 20 nm for both pH 9.3 and 11.7. Moreover, the particle size was lower than 100 nm when the silica content reached 25 g/l for pH 11.7, while the particle size had reached 755 nm when silica content was 20 g/l for pH 9.3. It seems that silica sol was more suitable in higher pH value.

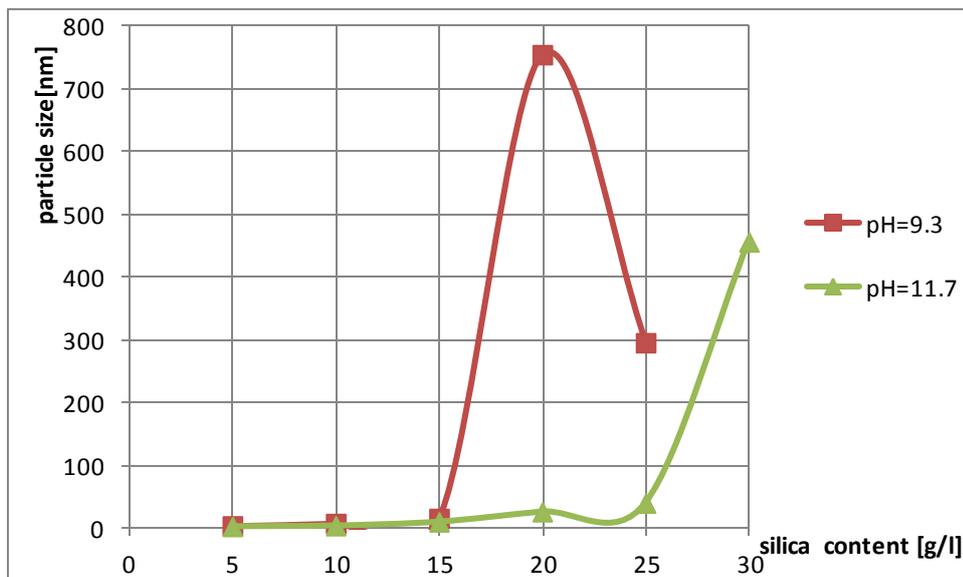


Figure 14. Particle size of silica sol prepared in pH=9.3 and pH=11.7, T= 25° C

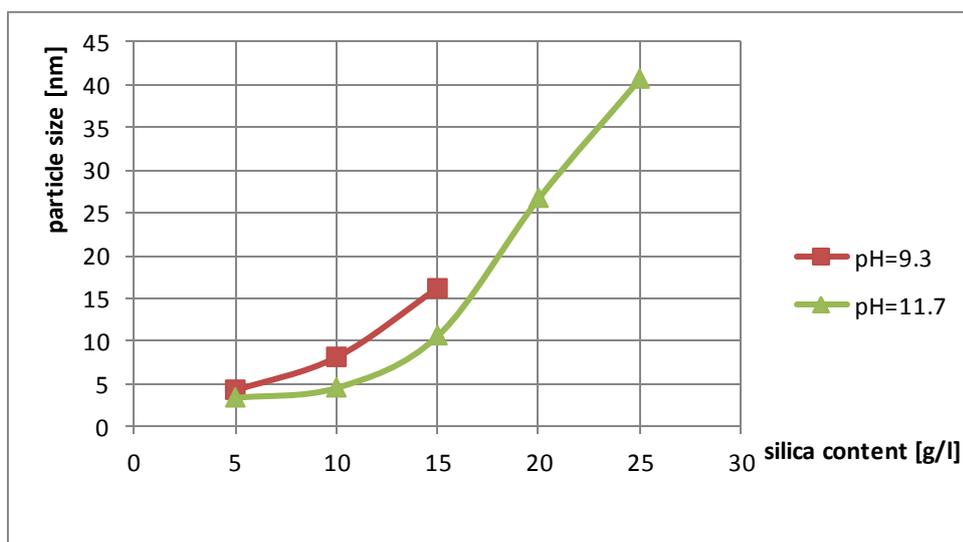


Figure 15. Particle size of silica sol prepared in pH=9.3 and pH=11.7, T= 25 °C

Zeta potentials of samples were measured under the same concentration of 5 g/l. The results of zeta potential of silica sol prepared in pH 9.3 and 11.7, T=25 °C are displayed in Figure 16. When pH=11.7, the absolute value of the zeta potential increased with increasing silica content in solution till silica content 20 g/l, and then decreased again maybe due to compression of the electric double layer [62].

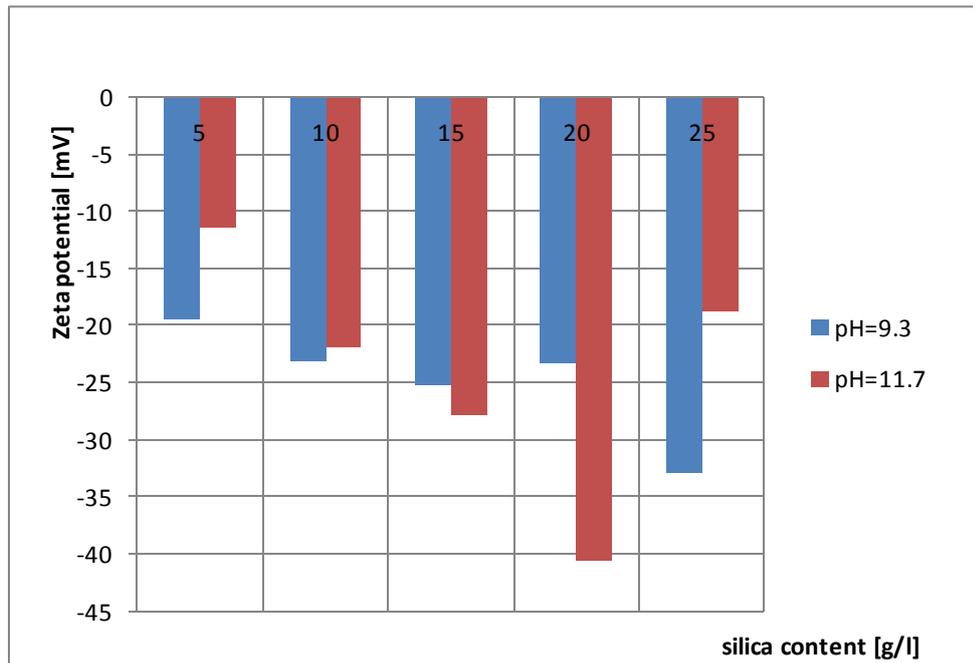


Figure 16. Zeta potential of silica sol (measured under 5 g/l) prepared in pH=9.3 and pH=11.7, T= 25 °C

5.2 Route from sodium silicate of synthesis of cellulose fiber-silica nanocomposite

5.2.1 Zeta potential

In the experiment, cellulose fiber-silica nanocomposites were both prepared from sodium silicate with $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$ and $2:1$. Figure 17 shows that the zeta potential of cellulose fiber-silica nanocomposites prepared from sodium silicate with $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$ and $2:1$. When composites were prepared from sodium silicate with $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$, zeta potential decreased with increasing target ratio of silica to fiber. On the other hand, pH value also had an effect on zeta potential. When cellulose fiber-silica nanocomposites were prepared from sodium silicate with $\text{SiO}_2:\text{Na}_2\text{O}=2:1$, the mixture of target ratio 1.5 and 1.8 gelled, when pH value was 9.3. However, no matter cellulose fiber-silica nanocomposites

prepared from sodium silicate with $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$ or $2:1$, zeta potentials of samples were lower in basic solution than that in acid solution.

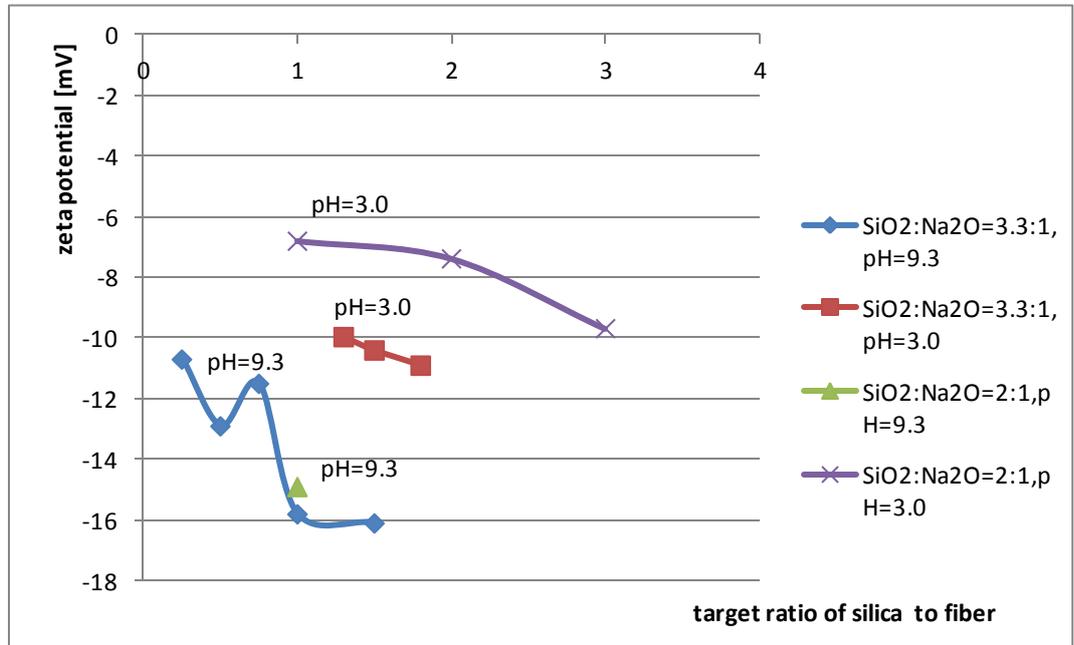


Figure 17. Zeta potential of cellulose fiber-silica nanocomposites with route from sodium silicate (measured under 0.3 g/l and EC 1.3 mS/cm)

5.2.2 Ash content measurement

When target ratio of silica to fiber was 1.3, 1.5 and 1.8, it means that target silica content in mixture was 57%, 60% and 64% respectively. As can be seen in Figure 18, the ash contents of mixture prepared with route from sodium silicate were below 1%, which was quite lower than target silica contents. Because of very low ash contents, accuracy of the results may be low. Estimated errors may be around 50 % of the result.

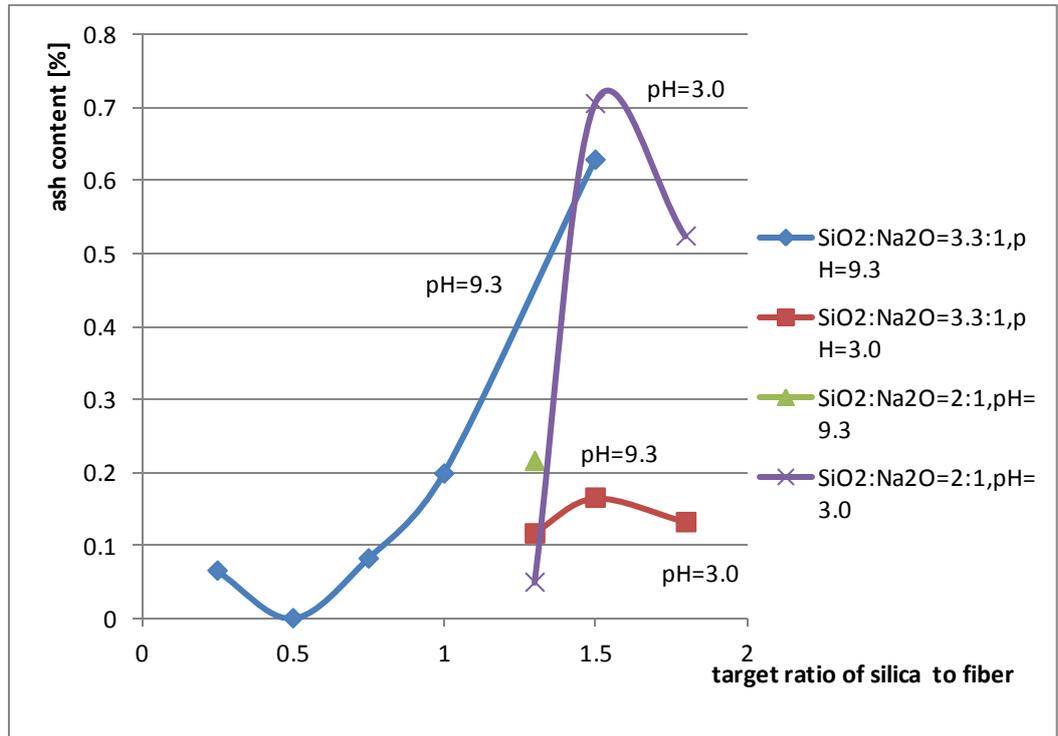


Figure 18. Ash content of cellulose fiber-silica nanocomposites with route from sodium silicate

5.2.3 SEM images of cellulose fiber-silica nanocomposite with route from sodium silicate

Figure 19 shows the SEM images of fibers (a) and cellulose fiber-silica nanocomposites with target ratio of silica to fiber 0.25(b) and 0.5(c), which prepared with sodium silicate of SiO₂:Na₂O=3.3:1, pH=9.3 and T= 25 °C. As can be seen, there was almost no silica deposited on the fiber surface.

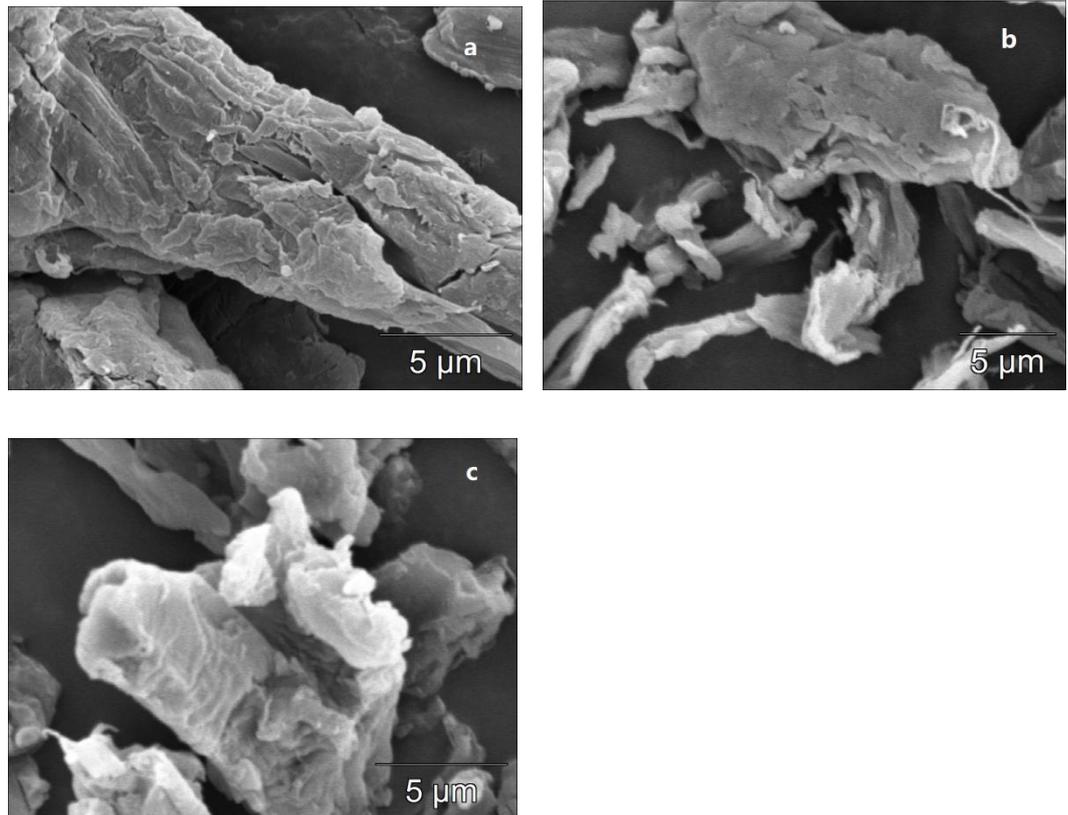


Figure 19. SEM images of fibers (a) and cellulose fiber-silica nanocomposites with target ratio of silica to fiber 0.25(b) and 0.5(c)

Figure 20 shows the SEM images of fibers (a) and cellulose fiber-silica nanocomposites with target ratio of silica to fiber 1.3(b) ,1.5(c) and 1.8(d), which prepared with sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$, $\text{pH}=3.0$ and $T=25\text{ }^\circ\text{C}$. It seems that the results were the same as described above, i.e. no precipitation onto the fibers. No matter in the basic or acidic environment, it was difficult to form obvious silica coating on the fiber surface.

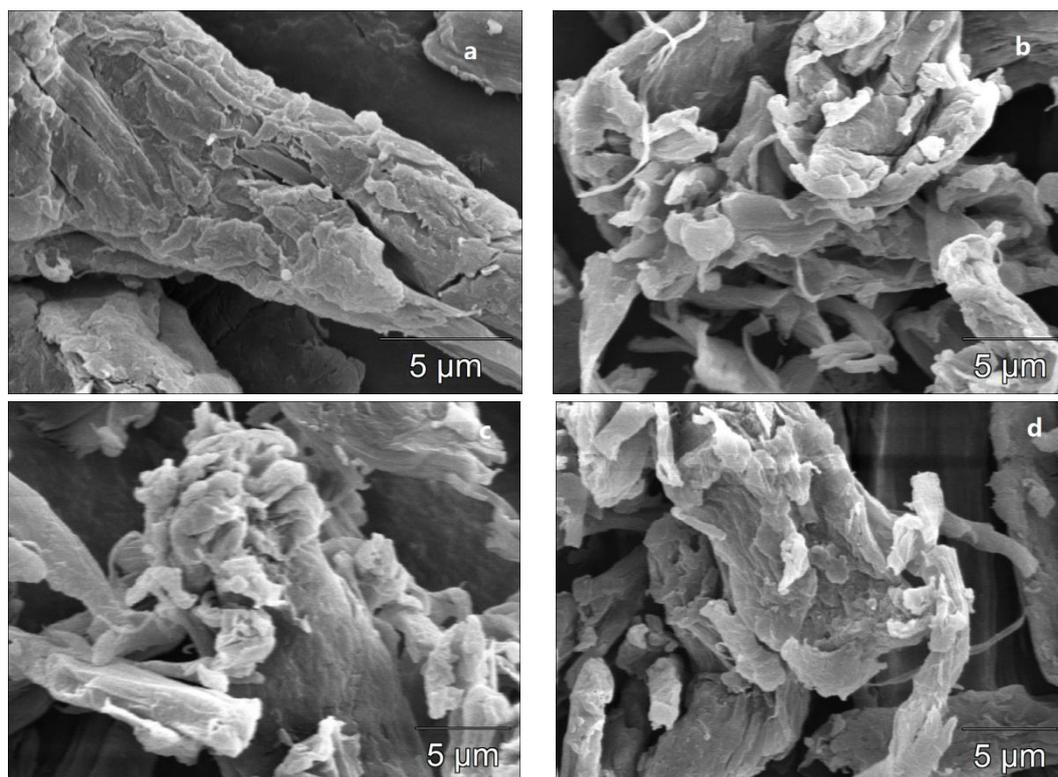


Figure 20. SEM images of fibers (a) and cellulose fiber-silica nanocomposites with target ratio of silica to fiber 1.3 (b), 1.5(c) and 1.8(d).

Figure 21 shows the SEM images of fiber (a) and hybrids prepared with sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}=2:1$, $T=25\text{ }^\circ\text{C}$, $\text{pH}=9.3$ (b) and $\text{pH}=3.0$ (c). It can be concluded that the types of sodium silicate had not much influence on the synthesis of cellulose fiber-silica hybrids.

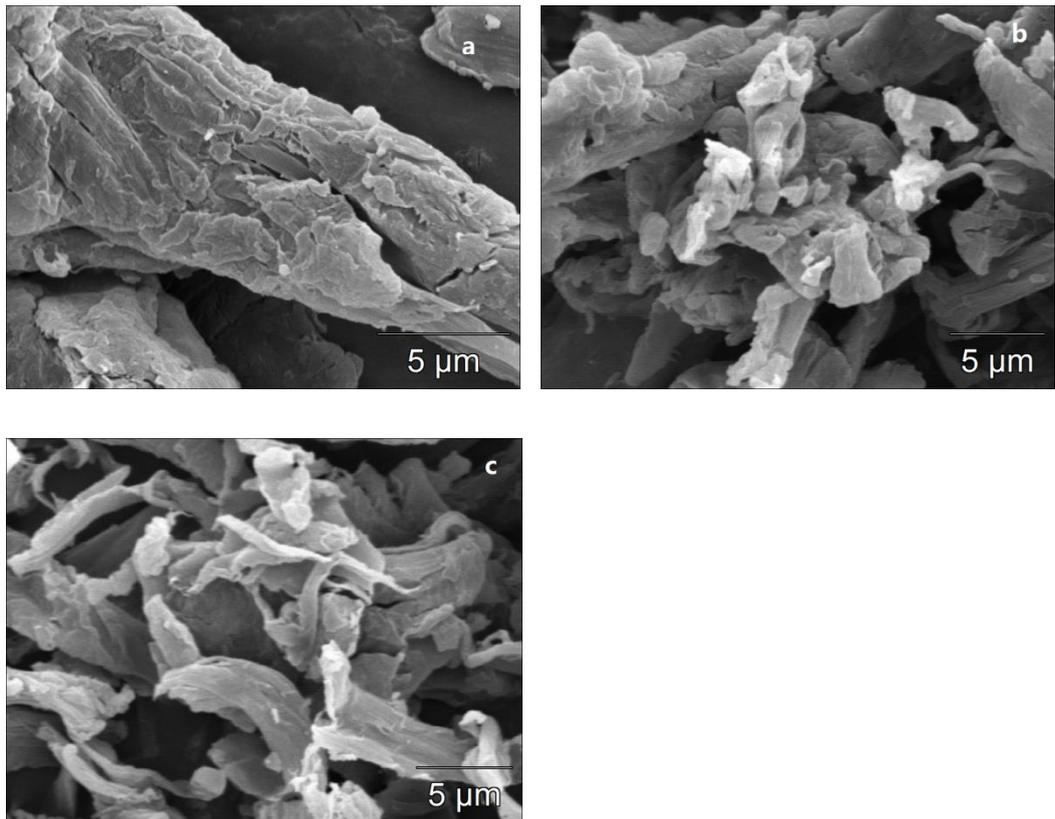


Figure 21. SEM images of fibers (a) and cellulose fiber-silica nanocomposites with pH=9.3 (b) and pH=3.0 (c)

Ash composition was analysed with scanning electron microscopy imaging, see figure 22.

Compared with Figure 22(a) and 22(b), it seems that hybrids which were synthesized in basic solution had small silica particles, connected with each other. However, on the other hand, hybrids prepared in pH 3.0, ash particles imaged were shaped like fibers. It means there was no silica particle on surface of this composite. Synthesized with different sodium silicate, Figure 22(c) shows that there were small amount of silica particles on the hybrids surface.

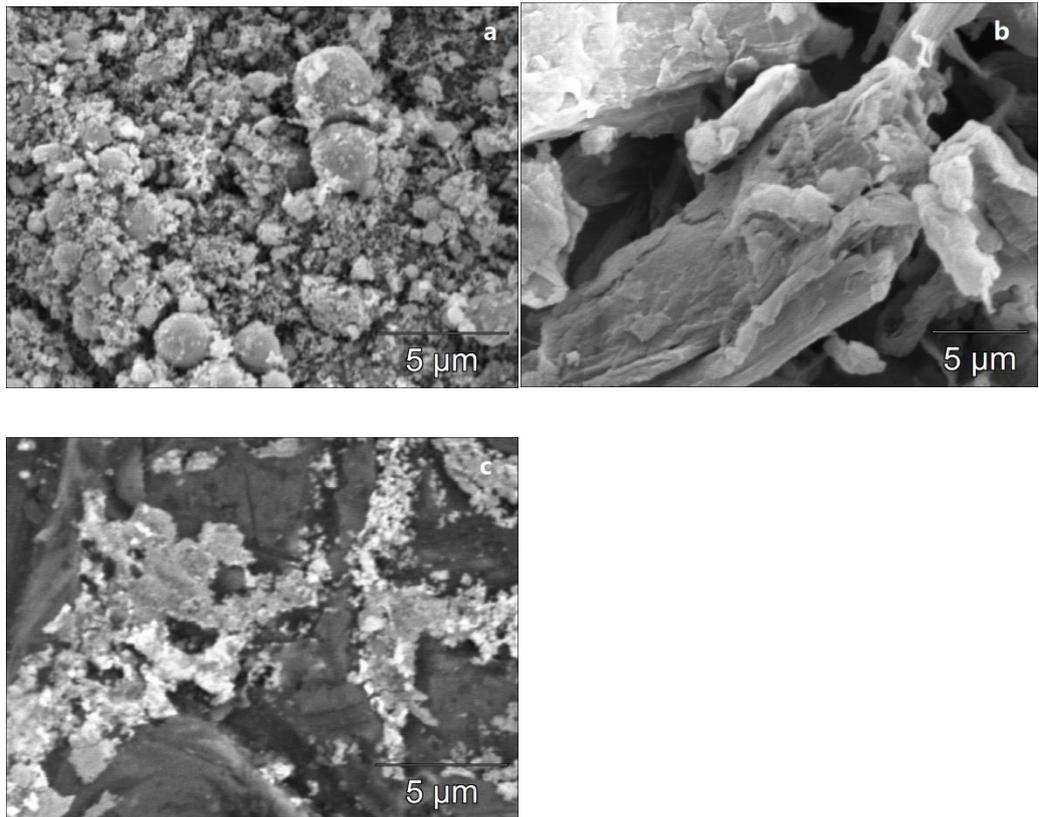


Figure 22. SEM images of ash of hybrids with target ratio of silica to fiber 0.25, sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$, $\text{pH}=9.3$, $T=25\text{ }^\circ\text{C}$ (a) , target ratio of silica to fiber 1.8, sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$, $\text{pH}=3.0$, $T=25\text{ }^\circ\text{C}$ (b) , and target ratio of silica to fiber 1.8, sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}=2:1$, $\text{pH}=3.0$, $T=25\text{ }^\circ\text{C}$ (c).

5.3 Route from silicic acid of synthesis of cellulose fiber-silica nanocomposite

In this experiment, composites were prepared with two types of sodium silicate solutions and different concentration of fiber in mixture solution. As can be seen in Figure 23, the zeta potential of cellulose fiber-silica composites were negative, which means that the surface of hybrids made from silicic acid was also negative charge. The zeta potentials were from -9 mV to -18 mV. It means that the composites were in incipient instability. The zeta potentials of cellulose fiber-silica composites made from sodium silicate with $\text{SiO}_2:\text{Na}_2\text{O}=2:1$ seemed not to change much even though with different target ratio of silica to fiber. From

1 to 2 of the target ratio, zeta potential was almost the same no matter what the concentration of fiber in mixture solution.

5.3.1 Zeta potential

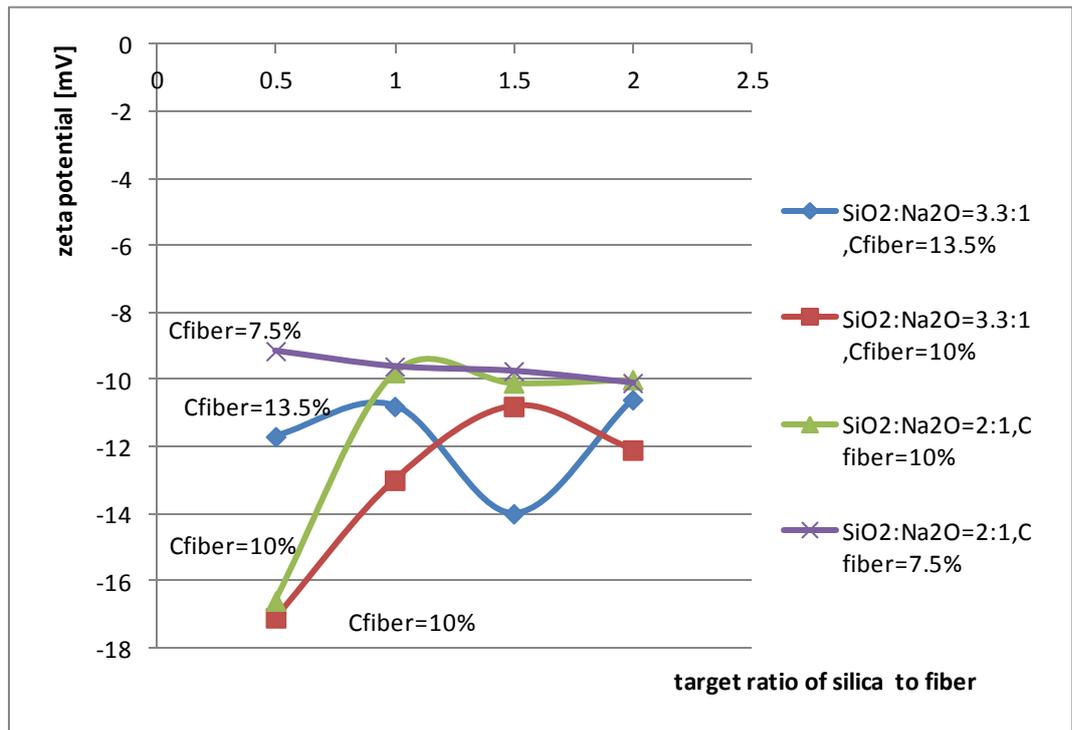


Figure 23. Zeta potential of cellulose fiber-silica nanocomposites with route from silicic acid (measured under 0.3 g/l and EC 1.3 mS/cm)

5.3.2 Ash content measurement

Figure 24 shows ash content of cellulose fiber-silica mixture with route from silicic acid as a function of target ratio of silica to fiber. When target ratio of silica to fiber was 0.5, 1, 1.5 and 2, it means that target silica content in mixture was 33.3%, 50%, 60% and 66.7% respectively. The ash contents of mixture were below 1.6 %, which were quite lower than target silica contents. When comparing the ash contents, the limitations in accuracy of measurements should be kept in mind. However, when compared with the results of Figure 18, the highest ash

content of mixture with route from silicic acid has reached to around 1.4 %, which was about twice of those prepared with route from sodium silicate.

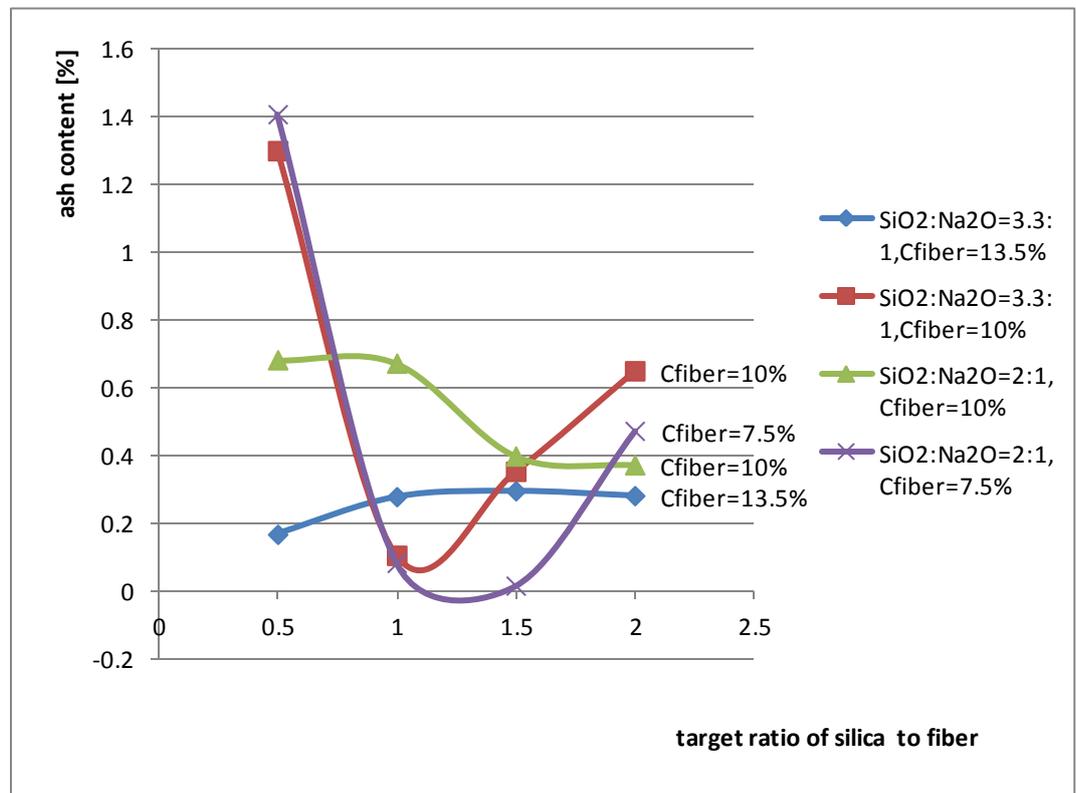


Figure 24. Ash content of cellulose fiber-silica nanocomposite with route from silicic acid

5.3.3 SEM images of cellulose fiber-silica nanocomposite with route from silicic acid

Figure 25 shows the SEM images of fibers (a) and cellulose fiber-silica nanocomposites prepared from sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$) with fiber concentration of 13.5 % (b) and 10% (c). It seems that it was not much different with fiber and hybrids which were prepared with route from silicic acid. The results of SEM images correspond to the value of ash content measurement. There was little silica particle adsorbed onto the fiber surface.

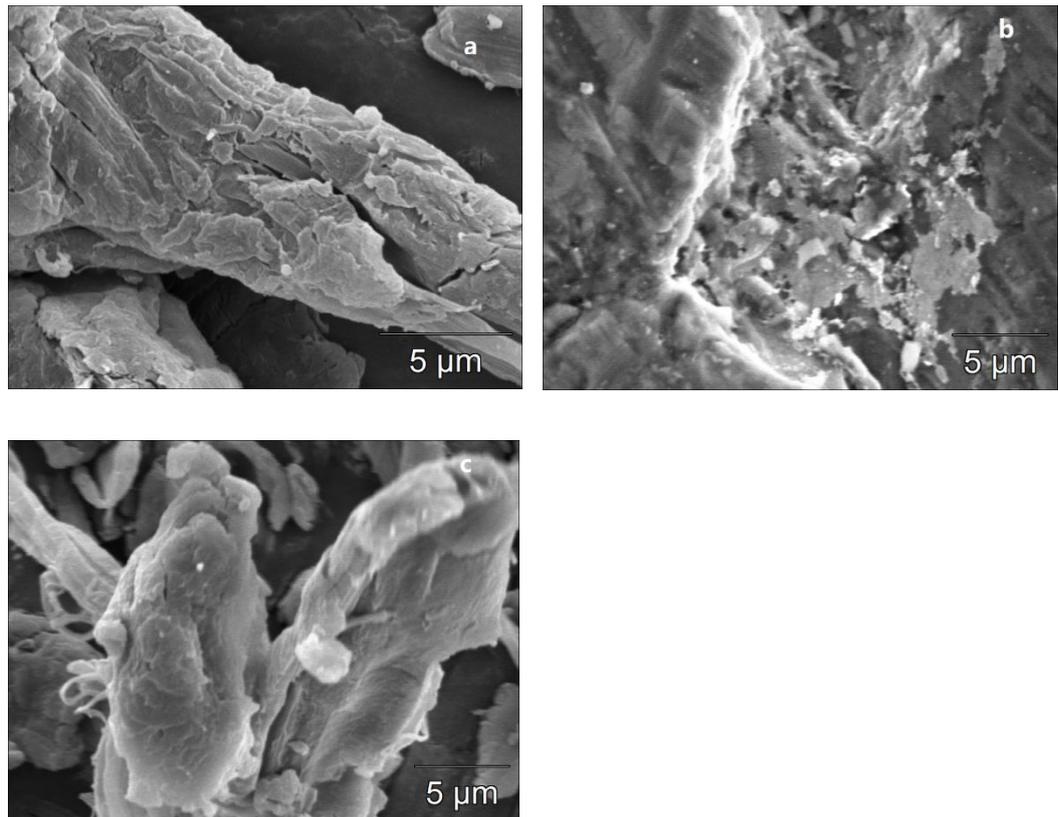


Figure 25. SEM images of fibers (a) and cellulose fiber-silica nanocomposites prepared from sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$) with fiber concentration of 13.5 % (b) and 10% (c)

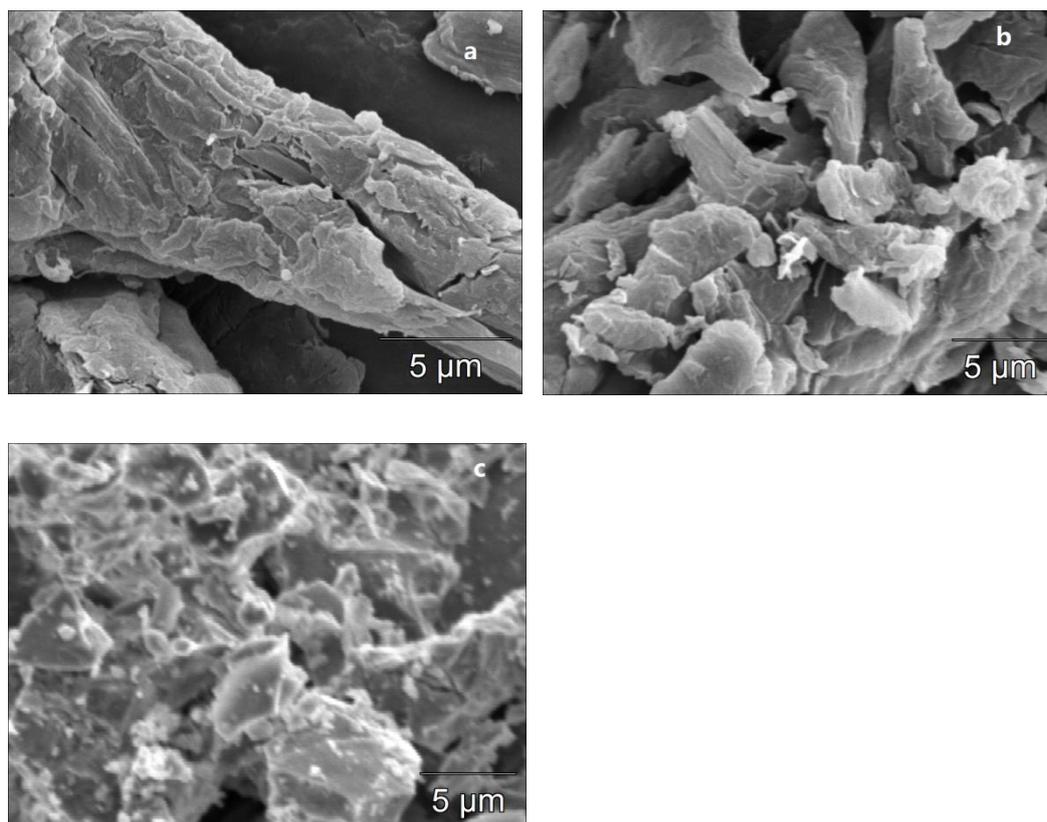


Figure 26. SEM images of fibers (a) and cellulose fiber-silica nanocomposites prepared from sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=2:1$) with fiber concentration of 10 % (b) and 7.5% (c)

It can be seen from Figure 26 that there was almost no silica particle on the fiber surface. Figure 25 and Figure 26 show the same result of route from silicic acid of synthesis of cellulose fiber-silica nanocomposites no matter what kind of sodium silicate was used.

Ash was analyzed with scanning electron microscopy measurement, see figure 27.

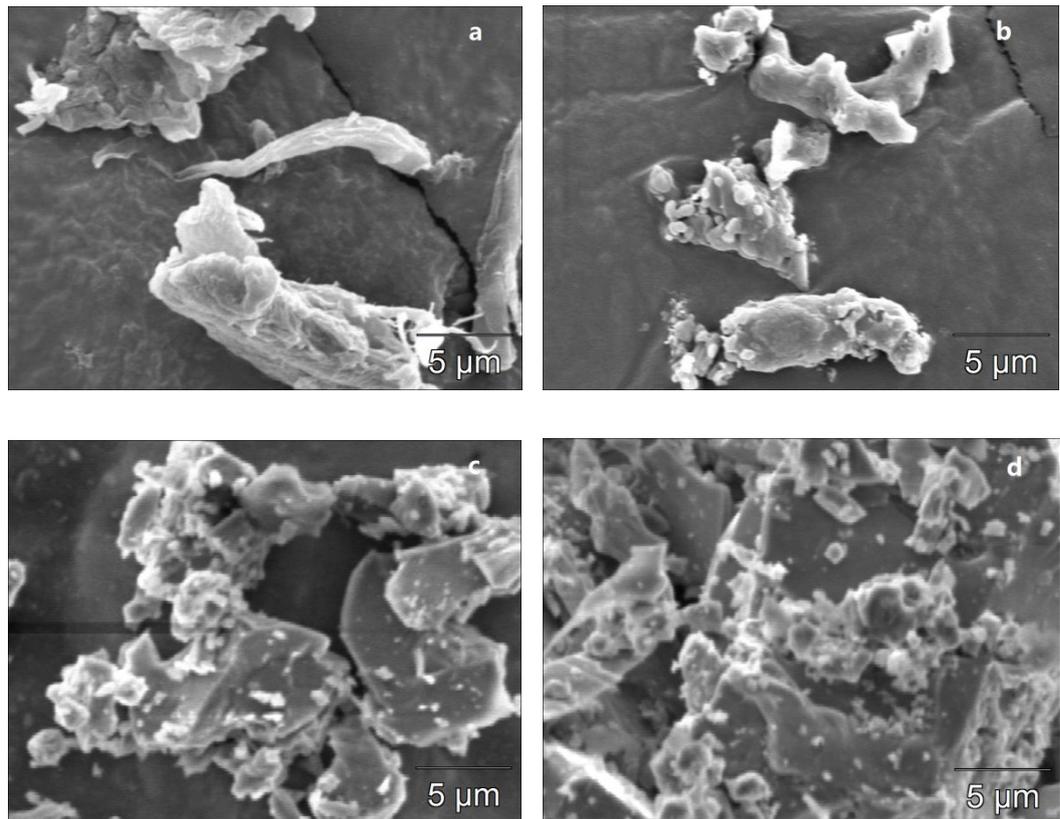


Figure 27. SEM images of ash of hybrids prepared from sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$) with fiber concentration of 13.5 % (a), prepared from sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$) with fiber concentration of 10% (b), prepared from sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=2:1$) with fiber concentration of 10% (c) and prepared from sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=2:1$) with fiber concentration of 7.5%

Compared with Figure 27 (a) and (b), it seems that ash still looks like fiber, not silica particles. However, Figure 27(c) and (d) shows that there were small amount of silica particles on the hybrids surface.

6 Conclusions

In this study, firstly nanosilica particles were prepared from sodium silicate and sulphuric acid. Then cellulose fiber-silica composites were synthesized with routes from sodium silicate or silicic acid.

In the experiment of preparing silica sol, it was concluded that the smaller particle size of silica particle could be made to higher target silica content in the more basic solution. When silica content reached 20 g/l, particle size of silica was around 27 nm at pH 11.7 while the size of silica had reached 755 nm at pH 9.3. Moreover, it was obviously observed that zeta potential of silica sol increased with increasing silica content.

After synthesis of cellulose fiber-silica mixtures, all the samples have been characterized by zeta potential, ash content measurement and SEM.

Zeta potentials of hybrids which were prepared with route from sodium silicate were lower in basic solution than that in acid solution, no matter what kind of sodium silicate with $\text{SiO}_2:\text{Na}_2\text{O}=3.3:1$ or $2:1$. When hybrids were synthesized with route from silicic acid, it seems that zeta potential was quite stable even with different target ratio of silica to fiber and did not change much comparing with those prepared with route from sodium silicate. All of the samples were around -16 mV.

According to the result of ash content measurement, it could be concluded that there were few of silica particles adsorbed onto the fiber surface. The highest ash content of samples was 1.4% when the target ratio of silica to fiber was 0.5 with route from silicic acid, which was about twice of those prepared with route from sodium silicate.

The results of SEM images of samples and ash correspond to the value of ash content measurement. Only few of silica particles could be observed on the fiber surface.

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